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PART II

DYNAMIC RESPONSE AND DAMPING BEHAVIOR OF HETEROGENEOUS POLYMERS

MAURICE MORTON, N. W. TSCHOEGL, and D. FROELICH
The University of Akron

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FOREWORD

This report was prepared by the University of Akron, Akron, Ohio, under USAF Contract Number AF33(615)-5008, "Dynamic Response and Damping Behavior of Heterogeneous Polymers." The contract was initiated under Project No. 7340, "Nonmetallic and Composite Materials," Task No. 734005, "Elastomeric and Compliant Materials," and was administered under the direction of the Elastomers and Coatings Branch, Nonmetallic Materials Division of the Air Force Materials Laboratory, with Dr. J. C. Halpin as Project Engineer. This report covers the period from 31 May 1967 to 30 June 1969.

This technical report has been reviewed and is approved.



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ABSTRACT

The mechanical properties of a polystyrene - 1,4-polybutadiene - polystyrene block copolymer of molecular weight 9500/37500/9500 were determined at temperatures between -60 and 130°C in sinusoidal shear over a frequency range from 25 to 1250 Hz, in tensile stress relaxation from -70 to 70°C over a time scale ranging from 1 to 1000 sec. and in tensile creep from -40 to 75°C over a time scale from 10 to 10,000 sec. The dynamic mechanical properties of a 1,2-polybutadiene - polystyrene block copolymer of molecular weight 160,000/40,000 were measured at ten temperatures, between -10 and 80°C over a frequency range from 250 to 2500 Hz. The dynamic measurements were made on compression molded specimens. The relaxation and creep data were obtained from solution cast samples.

These materials are not thermorheologically simple because the polystyrene - polybutadiene moieties of the molecules form separate microdomains, similar to, but smaller than the domains in polyblends. Empirically, the response curves obtained at different temperatures could be shifted into superposition and plots of the logarithmic shift factors against temperature showed qualitatively similar curves for each mode of measurement.

In the triblock copolymer the temperature dependence is dominated at low temperatures by the 1,4-polybutadiene moiety and at high temperatures by the polystyrene moiety. Because of the rather large difference in the respective glass transition temperatures (about 200°C) the two regions of dominance were quite well separated. At the lower temperatures, where the polystyrene domains essentially act as inert filler only, the temperature dependence could be well described by equations of the WLF form which were, however, different for the data derived from the dynamic and from the step function responses. The temperature dependence becomes dominated by the polystyrene domains above 59°C for the dynamic measurements and above 12.5°C for the step function response data. In this region the temperature dependence could be described by equations of the Arrhenius form with activation energies of 48 and 39 kcal/mole, respectively, superposed on the WLF equations describing the low temperature behavior. It is not clear at present whether these differences arise from the different time scales, from differences in the strain levels, or whether they reflect differences in the composition of the samples.

In the diblock copolymer the glass transition temperatures were not as widely separated (about 100°C). The temperature dependence at the lower temperatures could again be described by an

equation of the WLF form. At temperatures above about 30°C the WLF equation was no longer obeyed but it was not possible to obtain sufficient data for a more complete analysis because of the tendency of the material to flow.

The master curves for the triblock showed a remarkably extended pseudorubbery plateau between the two transition regions. Over this plateau damping was virtually constant but small ($\tan \delta \approx 0.25$). No such plateau appeared in the master curves for the diblock copolymer. Here the polybutadiene transition appeared to blend almost imperceptibly into a terminal flow region. The difference in the behavior of the tri- and diblock copolymers is readily explained by considering that the polystyrene domains act as crosslink points in the former, but as junction points for star-like clusters in the latter.

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DYNAMIC RESPONSE AND DAMPING BEHAVIOR
OF HETEROGENEOUS POLYMERS
N. W. Tschoegl and D. Froelich

INTRODUCTION

When a dynamic (sinusoidally oscillating) stress is applied to a polymeric substance and a measure of the mechanical loss (or energy absorption) is plotted as a function of frequency at constant temperature, the loss will evince a peak around a characteristic absorption (or damping) frequency. The peak is due to the dissipation of energy arising from the rearrangement of the long chain molecules as they tend to accommodate the imposed stress. Above the absorption frequency the stress varies too rapidly for the rearrangements to occur. Below it, the molecular rearrangements can take place in a leisurely fashion without much energy dissipation.

A similar loss peak occurs when the energy absorption is determined at constant frequency as a function of temperature. The interdependence between frequency and temperature is due to the effect of temperature on the relaxation times (rearrangement times) of the underlying molecular processes. The temperature at which the main chain motion of polymeric substances effectively ceases is called the glass transition temperature. It is characteristic of a given polymer and controls its mechanical damping properties.

In many applications of practical importance (such as vibration isolation, or acoustical damping) it is desirable that the loss peak should extend over as wide a range of frequencies or temperatures as possible. This can be achieved in principle by incorporating into the polymer molecule structural features associated with judiciously spaced loss mechanisms. Many polymers show secondary transitions apart from the primary glass transition. Thus polymers with relatively long side chains such as poly-n-butyl methacrylate¹ may show a transition arising from the motion of the side chains. However, the secondary loss peaks of homopolymers are normally too small to provide efficient damping.

Although exceptions have been noted², random copolymerization of monomers whose homopolymers would have different glass transition temperatures, generally leads to substances forming a single thermodynamic phase with a single intermediate transition temperature. The glass transition temperature, or T_g , of the random copolymer can usually be predicted from a knowledge of

the composition and of the T_g 's of the constituent homopolymers^{3,4,5}. However, block copolymers, composed of relatively long segments of homopolymers with different T_g 's, may show multiple glass transitions if the blocks are sufficiently dissimilar to form distinct thermodynamic phases. A similar effect can be achieved by simple physical blending of two dissimilar polymers⁶. However, in such blends phase separation is likely to occur on a macro scale⁷ leading to unstable systems.

The reason for phase separation and the formation of separate domains in blends is easy to see. The mixing of two phases is governed by the thermodynamic relation

$$\Delta G_m = \Delta H_m - T \Delta S_m \quad (1)$$

where ΔG_m , ΔH_m , and ΔS_m are changes in the free enthalpy (Gibbs free energy), the enthalpy, and entropy due to mixing, and T is the absolute temperature. For a long chain molecule ΔS_m is necessarily small. The change in the enthalpy of mixing of hydrocarbons is generally positive in the absence of specific strongly interacting groups. Thus ΔG_m , the change in the free enthalpy, is usually also positive, and mixing cannot occur.

Identical considerations apply to block copolymers whose constituents would not be miscible as homopolymers. Because the constituents are linked into one linear molecule, however, the size of the separate domains is dependent upon the chain lengths of the constituents and they are generally much smaller than the domains in blends of homopolymers. The existence of domains in block copolymers has been verified by electron microscopy.^{8,9,10}

The occurrence of separate domains has a profound influence on the mechanical properties of a block copolymer. Complete mechanical characterization of polymeric materials requires measurements over 10 to 20 decades of time or frequency. Such measurements cannot be made at a single temperature. To measure the mechanical properties (e.g. the damping) of polymeric materials over wide ranges of frequency, the device is commonly used of carrying out the measurements over a relatively restricted frequency range but at widely differing temperatures, and empirically shifting the response curves into coincidence along the logarithmic frequency axis. This principle of the equivalence of temperature and frequency is strictly valid only when all relaxation mechanisms are equally affected by a change in temperature. Its experimental validity has been demonstrated on a series of amorphous homopolymers and random copolymers. Such materials are termed thermorheologically simple materials.

Block copolymers with distinct multiple transitions are not thermorheologically simple. Since the relaxation mechanisms characteristic of the constituent blocks will be associated with separate distributions of relaxation times, the simple frequency-temperature (or time-temperature) superposition practiced with linear amorphous polymers must fail in the case of block copolymers.

The purpose of the research reported here was to obtain information on time-temperature superposition on polymers with multiple transitions.

MATERIALS

Two materials were examined: a polystyrene - 1,4-polybutadiene-polystyrene triblock, and a 1,2-polybutadiene-polystyrene diblock copolymer. The first was a commercial product, Shell Kraton 102. The second was prepared at the University of Akron and contained 1% of N-phenyl-2-naphthylamine. It will be identified in the figures by the symbols SB 40/160. Kraton 102 contains about 0.25% of antioxidant (Ionol) but is otherwise said to consist of the block copolymer only¹¹. No work appears to have been reported on Kraton 102 although some related materials, Shell Kraton 101, Shell T226 and T125, have been investigated^{12, 13}. The molecular weight of Kraton 102 is lower than that of Kraton 101¹⁴. We chose Kraton 102 because we expected it to be more readily moldable than Kraton 101¹¹. Shell T226 and T125 contain a plasticizer, a dye, and possibly other additives¹².

Sequence Length

A gel permeation chromatogram of Kraton 102 (0.5 percent weight per volume in tetrahydrofuran, lcc/min.) is shown in Fig. 1. It shows a single peak and only a small broad shoulder at the low molecular weight tail. The latter may represent a small amount of polystyrene.

The number average molecular weight of Kraton 102 in toluene as determined in a Melabs Membrane Osmometer was 56500. The styrene content was determined as 33% by NMR spectroscopy. A separate determination by the method of Kolthoff, Lee and Carr,¹⁵ in which the polybutadiene moiety is cleaved off by oxidation and the remaining polystyrene is weighed, gave 31%. From these figures, the number average molecular weight of the polystyrene moiety is estimated as 9500 and that of the polybutadiene moiety as 37,500.

The diblock copolymer had a number average molecular weight of 200,000 with a styrene content of 20 percent by weight, as determined at the University of Akron. The number average molecular weight of the polystyrene moiety therefore was 40,000, and that of the polybutadiene moiety 160,000.

Glass Transition Temperature

The lower (1,2-polybutadiene) glass transition temperature of the diblock copolymer as determined at the University of Akron by differential scanning calorimetry (DSC) was - 8°C. The lower (1,4-polybutadiene) transition temperature of the triblock, Kraton 102, was - 88°C by differential thermal analysis (DTA) on

our Dupont Thermal Analyzer at a heating rate of 5°C/min., both for a compression molded sample, and one that was cast from solution in benzene.

The upper (polystyrene) transition temperature of the diblock was obtained with some difficulty as 100°C by DTA. The upper transition temperature of the triblock could not be determined reliably. Torsion pendulum measurements at around 0.1 Hz indicated a peak in the $\log \tan \delta$ curve at about 80°C. Differential thermal analysis in the Dupont Thermal Analyzer as well as differential scanning calorimetry¹⁶ in a Perkin-Elmer Scanning Calorimeter revealed no transition, but showed an endothermic peak at 83°C which could be due to a stress release which is sometimes observed on a glass transition¹⁶. This value agrees well with the value of 84°C found by Canter¹³ using Perkin-Elmer and Leeds and Northrup differential thermal calorimeters for the upper transition of the related block copolymer in Shell Tl25.

A value of about 83°C for the glass transition of polystyrene chains of molecular weight 10,000 is not unreasonable but rather lower than what one would calculate from the equations of Fox and Flory²⁰, and Ueberreiter and Kanig²¹, taking into account that the polystyrene chains have only one free end each¹³.

Attempts to determine the upper glass transition by measurements of the temperature dependence of the linear expansion coefficient of a small cylindrical specimen using a linear variable differential transformer (LVDT) failed because the material softened at about 50°C and the specimen deformed even under the small pressure of the LVDT core. No transition was found between 10° and 80°C in refractometric measurements in which a film of the triblock copolymer was cast directly onto the prism of a Bausch and Lomb refractometer. This refractometric method has been used successfully by several authors^{17,18,19} for determining glass transitions in polyblends and block copolymers. The measurements could not be extended to higher temperatures because of apparatus limitations. They were carried out to demonstrate that there was no transition in the region between 10° and 80°C in which a change (to be discussed later), occurred in a plot of the empirical temperature shift factors, $\log a_T$, against the temperature.

The difficulty in locating the glass transition of the polystyrene moiety in the Shell block copolymers, already emphasized by Canter¹³, might appear to be due to the short chain length and relatively low percentage. It appears that mechanical methods are the most sensitive for the determination of the upper glass transition in block copolymers containing short polystyrene end blocks. It is interesting to note that Canter¹³ found the transition to become sharper (without shifting its location) when the specimen was pre-stretched.

EXPERIMENTAL

The dynamic mechanical properties of the two block copolymers

were measured on compression molded disc-shaped specimens. The results are reported in detail below. Results will also be discussed which were obtained in measurements on Kraton 102 in uniaxial tension in relaxation and in creep on solution cast strip specimens. The experimental details of these measurements will be reported elsewhere²⁰.

Methods

The dynamic measurements proved rather difficult. They were made on a Ferry-Fitzgerald apparatus,^{21,22} and a large number of determinations had to be made since it was necessary to repeat much of the data for varying experimental reasons. Specimens of different size must be used in different temperature regions to obtain the best results.

The measurements on Kraton 102 reported here were made on three different twin specimens. Two twins, A and C, had diameters of about 0.95 cm and heights of about 0.5 cm. Determinations were made on these specimens at ten temperatures each between -60 and 30°C at frequencies from 25 to 798 Hz. Twin specimens B, which had diameters of about 1.9 cm and heights of about 0.34 cm, were used for twenty-one temperatures between 30 and 130°C at frequencies from 25 to 1,260 Hz.

Relaxation measurements were made in uniaxial tension at a fixed strain of 4 percent at sixteen different temperatures between -70 and 70°C on 10 x 1 x 0.2 cm strip specimens. The strips were cut from sheets cast from solutions of Kraton 102 in benzene.

The tensile creep measurements were made at eleven different temperatures between -40 and 75°C at fixed loads acting on 20 x 1.27 x 0.12 cm strips cut from a sheet cast from benzene solution. The loads were kept small enough so that the final strains were generally between 2 and 8 percent.

The dynamic measurements on the diblock copolymer were made on two twin specimens. Twin specimens S had the same diameters as specimens A and C. Determinations were made on these specimens at six temperatures between -9.9 and 5.5°C, at frequencies between 250 and 2500 Hz. Specimens M had diameters of about 1.9 cm and lengths of about 0.30 cm. Determinations were made on specimens M at thirteen temperatures between 9.1 and 78.5°C at the same frequencies.

A nitrogen blanket was used whenever measurements were made at temperatures above 50°C to prevent oxidation of the samples. Following measurements at elevated temperatures, checks were made frequently at lower temperatures to ascertain that the specimen properties had not changed.

Sample densities were calculated from

$$\rho = \rho_0 [1 - \alpha (T - T_0)] \quad (2)$$

where ρ is the density, T the temperature, and α the cubical thermal expansion coefficient. The subscript refers to the reference density and temperature, respectively. The thermal expansion coefficient of both materials was taken as 0.0006 deg.^{-1} .

Specimen Preparation

For the measurements of the dynamic properties on the Ferry-Fitzgerald apparatus it was necessary to prepare cylindrical and disc-shaped specimens of precise shape. Considerable trouble was experienced in the preparation of suitable specimens by compression molding. The discs were always distorted and never free of bubbles even when the material was carefully dried in a vacuum oven before molding and was remolded after a first compression. In an attempt to arrive at a suitable molding procedure, a number of experiments were made on Shell Kraton 102 in which the processing variables (temperature, pressure, and time) were varied systematically. These attempts proved fruitless. This refractoriness appears to be due to the differences in the thermal expansion coefficients and the compressibilities of the polystyrene and polybutadiene domains in the block copolymers^{1,2}.

Satisfactory specimens were finally obtained from Kraton 102 by molding under vacuum while the temperature and pressure were kept as low as possible. Special vacuum molds were constructed for this purpose. They consist of precision bored stainless steel cylinders which may be closed by a screw-in plug at the bottom and a tight-fitting piston at the top. The bore of the cylinder is determined by the desired diameter of the specimen. The upper surface of the plug and the lower surface of the piston are carefully machined to produce a disk with plane-parallel endfaces. About two-thirds from the bottom the cylinder bears a side arm through which it may be evacuated.

The molding procedure is as follows: The cylinder, piston, and plug are cleaned to remove any traces of material which might adhere to the surfaces as a result of the previous molding. The cylinder is then closed at the bottom, and a weighed amount of the material is introduced from the top. The amount of the material determines the height of the specimen. Since two identical specimens must be installed in the apparatus simultaneously, the amount must be carefully controlled.

The cylinder is immersed about halfway in an oil bath, and the top is closed by inserting the piston and moving it just above the opening of the side arm. The vacuum pump is then connected to the side arm and the cylinder is evacuated for about 10 minutes at room temperature. Maintaining a constant vacuum,

the temperature of the bath is raised to the molding temperature, ($\sim 30^{\circ}\text{C}$) and kept there for 30 minutes. A slight pressure is then applied (either by hand, or by a suitable weight), released, and reapplied for 10 minutes. After the vacuum is broken, the mold is removed from the bath and cooled. Finally the bottom plug is unscrewed, and the test piece is extruded with the help of the piston. Kraton 102 specimens could be extruded at room temperature. The specimens were transparent but showed a slight iridescence. Diblock copolymer specimens could be extruded successfully only when the mold was cooled to -15°C .

RESULTS

Figure 2 shows a plot of the storage compliance, $J'(\omega)$, of Kraton 102 against the frequency, ω , on a doubly logarithmic plot at ten selected temperatures between the lowest (-60°C) and the highest (129.9°C) temperature. The storage compliances were reduced to the reference temperature, 30°C , using the equation^{2,2}

$$J_p'(\omega) = (T_p/T_0\rho_0)J'(\omega) \quad (3)$$

and were then shifted into superposition. Because of the scatter, the loss data could not be superposed in this way. The shift factors, $\log a_T$, obtained from shifting the storage compliances, are shown in Table I. A plot of the shift factors is shown in Fig. 3. Smoothed data taken from this plot were used to construct the master curves for both $J_p'(\omega)$ and $J_p''(\omega)$ shown in Figs. 4 and 5. Similar master curves were obtained^p also for the storage modulus, $G_p'(\omega)$, and the loss modulus, $G_p''(\omega)$. These are shown in Figs. 6 and 7. To avoid overcrowding of the data points, not all data actually obtained are shown in these plots. In the temperature key for the plots the highest temperature for a particular symbol is designated by a pip pointing up. Successive 45° clockwise rotations of the pip denote successively lower temperatures. The key (cf. Table I) is as follows: Specimen B: open circles, pip outside: 129.9° to 94.8°C ; pip inside: 89.6° to 55.5°C ; circles with lower half filled: 50.0° to 30.0°C ; specimen C: circles with lower half filled, 29.4° to 19.9°C ; upper half filled: 15.0° to -24.9° ; Specimen A; left half filled: 4.6° to -60°C .

Also shown in Figs. 4 to 7 are the dynamic data calculated from the step function responses obtained on the solution cast samples. The tensile relaxation modulus, $E(t)$, and tensile creep compliance, $D_c(t)$, were first converted^p into the corresponding shear responses using the customary factor of 3. The dynamic data were then calculated from the shear responses by the method of Yagii and Maekawa^{2,3}.

Figure 8 shows a plot of the loss tangent,

$$\tan \delta = J''(\omega)/J'(\omega) = G''(\omega)/G'(\omega) \quad (4)$$

derived from the smoothed curves in Figs. 4 and 5.

Figures 9 to 12 show the master curves for the storage compliance, loss compliance, storage modulus, and loss modulus of the diblock SB 40/160 obtained from the dynamic data for a reference temperature of 25°C . The storage and loss compliances were shifted simultaneously to reduce the ambiguity arising from scattered data. The empirical shift factors are tabulated in Table II and plotted in Fig. 13.

TABLE I

Temperature Shift Factors, $\log a_T$, for Kraton 102

<u>Specimen A</u>		<u>Specimen B</u>	
<u>$\log a_T$</u>	<u>Temp. ($^{\circ}\text{C}$)</u>	<u>$\log a_T$</u>	<u>Temp. ($^{\circ}\text{C}$)</u>
0	30.5*	0	30.0
0.4	20.0*	-0.1	35.0
0.8	10.0*	-0.1	39.6
1.0	4.6	-0.4	45.3
1.3	-8.5	-0.6	50.1
1.6	-18.0	-0.9	55.5
2.0	-30.0	-1.1	59.6
2.4	-39.0	-1.6	65.2
2.85	-48.5	-2.2	70.0
3.5	-60.0	-2.4	75.0
		-2.8	79.4
		-3.5	85.3
		-3.8	89.6
		-4.2	94.8
		-4.8	99.9
		-5.2	105.0
		-5.6	109.8
		-5.9	114.8
		-6.1	119.5
		-6.3	124.9
		-6.5	129.9
<u>Specimen C</u>			
<u>$\log a_T$</u>	<u>Temp. ($^{\circ}\text{C}$)</u>		
0.1	25.7		
0.2	19.9		
0.4	15.0		
0.6	4.7		
0.7	0		
1.0	-4.8		
1.2	-9.7		
1.6	-14.7		
1.8	-20.3		
1.9	-24.9		

* Not used in construction of master curves.

TABLE II

Temperature Shift Factors, $\log a_T$, for SB 40/160

<u>Specimen M</u>		<u>Specimen S</u>	
<u>$\log a_T$</u>	<u>Temp. ($^{\circ}\text{C}$)</u>	<u>$\log a_T$</u>	<u>Temp. ($^{\circ}\text{C}$)</u>
-1.99	78.5		
-1.79	68.9	1.50	5.5
-1.56	60.3	1.74	2.7
-1.29	51.2	2.41	0
-1.11	39.9	2.74	-1.9
-0.72	34.7	3.61	-6.7
-0.47	29.4	5.01	-9.9
0	24.8		
0.29	22.4		
0.35	22.0		
0.58	18.2		
0.88	15.5		
1.38	9.1		

Smoothed data read from the curve were used to construct the master curves.

The temperature key for the master curves is as follows:
 Specimen M: circles with left half filled: 78.5, 68.9, 60.3, 51.2, 39.9, 34.7, 29.4, 24.8 $^{\circ}\text{C}$; open circles: 22.4, 22.0, 18.2, 15.5, 9.1 $^{\circ}\text{C}$; Specimen S: circles with lower half filled: 5.5, 2.7, 0, -1.9, -6.7, -9.9 $^{\circ}\text{C}$.

DISCUSSION

The relaxation modulus and creep compliance data on Kraton 102 had shown very little scatter and could be shifted smoothly into superposition along the logarithmic time axis²⁰. These data covered three to over four decades of time at each temperature. The dynamic data extended only over a little more than 1.5 decades at a given temperature and showed considerable scatter. Nevertheless, they could be superposed with some difficulty. The fanning-out of the shifted data which is so conspicuous in the master curves for SB 40/160, was absent in the Kraton data. As shown in Fig. 3, the temperature dependence of the storage compliances of Kraton is complex, showing a distinct change around 55 $^{\circ}\text{C}$. The curve shows some resemblance to that reported by Beecher et al¹⁰ for a polystyrene-polyisoprene-polystyrene triblock copolymer of molecular weight 130,000.

At the lower temperatures (up to about 55°C) the temperature dependence of $J'(\omega)$ for Kraton 102 could be well described by the equation

$$\log a_T = - \frac{7.72 (t - 30)}{291.0 + t - 30} \quad (5)$$

The values of the constants were obtained from the slope and intercept²² of a plot of $(t-30)/\log a_T$ against $(t-30)$. Equation (5) is very similar to the equations obtained by Kraus and Gruver²⁴ and by Mancke²⁵ for a 1,4-polybutadiene of, presumably, similar microstructure to that of the polybutadiene moiety in Kraton 102. The equations of Kraus and Gruver, and of Mancke, when referred to the same reference temperature as Eq. (5), give logarithmic shift factors which are only about 0.3 logarithmic units lower than those obtained from Eq. (5) at temperatures below about 0°C. Thus the temperature dependence of the dynamic mechanical properties of Kraton 102 appear to be dominated almost completely by the rubbery moiety up to about 55°C. In this temperature region the glassy polystyrene acts primarily as an inert filler and contributes to the temperature dependence only by slightly increasing the shift factors. A similar effect was noted by Horino et al.⁶ in polymer blends.

The shift factors, $\log a_T$, begin to deviate noticeably from those predicted by Eq. (5) at temperatures above about 55°C. Up to about 80° - 100°C the polystyrene domains in the block copolymer must still be essentially glassy. We therefore subtracted the values of $\log a_T$ (WLF) calculated from Eq. (5) from the empirical shift factors, $\log a_T$ (EXP), and plotted the differences against the reciprocal absolute temperature. The resulting Arrhenius plot is shown in Fig. 14. The data for the temperature region between about 60 and 100°C lie sensibly on a straight line, from which the apparent activation energy, ΔH_a , is obtained as 48.2 kcal/mole. This is in fairly good agreement with the value of 40 kcal/mole calculated from the data by Smith and Dickie¹² for Kraton 101. The line intersects the abscissa at 59.1°C. This value may be regarded as the temperature, T_0 , at which the contribution of the polystyrene moiety to the temperature dependence of the mechanical properties of the block copolymer becomes noticeable. The overall temperature dependence could therefore be described by an equation of the WLF form up to T_0 , and above T_0 by an equation of the Arrhenius form superposed on the WLF equation. The solid line in Fig. 3 represents the equation

$$\log a_T = - \frac{c_1 (T - T_{\text{ref}})}{c_2 + T - T_{\text{ref}}} h(T) + \frac{\Delta H_a}{2.303 RT} \left(\frac{1}{T} - \frac{1}{T_0} \right) h(T - T_0) \quad (6)$$

where T is the absolute temperature, R is the gas constant, $h(T)$ is the unit step function,²⁶ c_1 , c_2 , and T_{ref} have the values

given by Eq. (5), and ΔH_a and T_0 have the values shown in Fig. 14.

At temperatures above about 100°C the temperature dependence departs from the behavior predicted by Eq. (6) because in this region the polystyrene contribution can no longer be described by an Arrhenius equation. In principle a third term, again of the WLF form, could be added to Eq. (6) to describe the temperature dependence of the polystyrene in the transition region, but our data were insufficient for a determination of the required parameters. Alternatively, an equation such as that recently proposed by Rusch^{27, 28} could replace both the Arrhenius and the second WLF term by a single term to describe the contribution of the polystyrene both in the glassy and the transition region. Rusch showed^{27, 28} that the temperature dependence of the mechanical behavior of polystyrene could be described by the equation

$$\log a_T = - \frac{c_1 (T_e - T_{ref})}{c_2 + T_e - T_{ref}} \quad (7)$$

where T_e is the "effective" temperature of the glass²⁷. An attempt to use Rusch's data for our case was not highly successful probably because the behavior of the polystyrene moiety in the block polymer is not adequately described by data obtained on a polystyrene homopolymer of considerably higher molecular weight.

The temperature dependence of the relaxation and creep data obtained on Kraton 102 sheets cast from benzene solution showed qualitatively similar behavior²⁰ to that shown in Fig. 14. It is reproduced in Fig. 15. As a comparison of Figs. 3 and 9 shows, the lower temperature portion of the temperature dependence of $\log a_T$ is quite different for the data derived from the dynamic tests on the one hand and the relaxation and creep tests on the other. The lower temperature portion of the data in Fig. 9 could be fitted by a WLF equation with $c_1 = 3.61$, $c_2 = 224^\circ\text{C}$, and $t_{ref} = 100^\circ\text{C}$. When the shift factors obtained from the WLF equation were subtracted from the experimentally determined ones and the differences were plotted against the reciprocal temperature,²⁰ a value of 39.1 kcal/mole was obtained for ΔH_a , and a value of 12.5°C for T_0 . The solid line through the data in Fig. 15 represents Eq. (6) with the parameters stated above. Because the shift factors plotted in Fig. 15 change more rapidly with temperature than do the shift factors plotted in Fig. 3, the dynamic data calculated from the master curves of $E_p(t)$ and $D_p(t)$ are considerably flatter than the master curves obtained from the dynamic tests directly. This is evident in Figs. 4 through 7.

The easiest explanation of the differences in the behavior in the dynamic tests and the relaxation and creep tests is to consider that the two samples were not identical.

The dynamic tests were performed on specimens which were compression molded from material that had been obtained from solution in an unknown solvent. By contrast the relaxation and creep tests were conducted on specimens cut from sheets cast from benzene solution. Since benzene is a good solvent for both polybutadiene and polystyrene it is at least conceivable that the polybutadiene phase in the solvent cast specimen may contain some polystyrene and, conversely, the polystyrene domains may contain some polybutadiene. This would result in a lowering of T_0 and in making the lower temperature portion of the temperature dependence a steeper function of the temperature. Polystyrene molecularly dispersed in the polybutadiene regions would make these regions behave similarly to an SBR of the same composition. The temperature dependence of SBR generally follows the "universal" form of the WLF equation^{22, 29}. Matching the experimental data to a curve of this form yields a characteristic temperature, T_s , of -29°C , hence a T_g of approximately -79°C . The value measured by DTA was -88°C . The difference in the two glass temperatures is not easily explained. Besides, the same value of -88°C was also obtained by DTA on the compression molded sample, indicating that the composition of the polybutadiene domains in the two samples must have been identical. Some work is currently under way in our laboratory using electron microscopy and small angle x-ray scattering in an attempt to ascertain whether the domain structure in the two samples differs.

It is also possible that the differences in the behavior observed in the dynamic and the step function responses arises from the different amounts of strain to which the specimens were subjected. In the dynamic tests the maximum shear strain was of the order of 0.4%. In the relaxation and creep tests the specimens were subjected to a tensile strain of about 4%. According to the data of Holden, Bishop, and Legge³⁰, the polystyrene domains are not likely to be disrupted at this level of strain for a triblock copolymer containing about 30 - 33% styrene, but this possibility should not be dismissed without further tests.

If neither differences in the level of strain or in the composition of the two specimens are responsible for the observed discrepancies, the possibility must be considered that T_0 as well as the general form of the temperature dependence of the shift factors is a function of the experimental conditions, i.e. of the time scale of the experiment³¹. In the latter case a master curve would be illusory and time-temperature superposition, although feasible empirically, would be meaningless as a means of predicting behavior at a given temperature from behavior at another.

Experimentally the simplest way to settle this question would be the determination of the mechanical properties of both

samples in identical experiments. Unfortunately, we were unable to cut the specimens for the Ferry-Fitzgerald apparatus from cast sheets because of experimental difficulties of cutting small cylinders of precise geometry. At the same time we had no means to compression mold specimens by our vacuum technique to cut strips for relaxation or creep tests. We are now trying to resolve the problem by carrying out measurements in a dynamic shear rheometer²⁰ in which we will be able to conduct measurements over a frequency range from 0.05 to 1000 Hz (i.e. over almost 4.5 decades in contrast to the 1.5 decades achievable in the Ferry-Fitzgerald apparatus) and at temperatures ranging from about -70 to 150°C.

If we accept, for the time being, the position that the two samples on which the dynamic and the step function response measurements were made, differ in their properties, we may infer that in a triblock copolymer with widely spaced glass transitions such as Kraton 102 the temperature dependence of the mechanical properties is dominated by the rubbery moiety of the block copolymer up to a characteristic temperature, T_0 , at which the contribution of the glassy moiety becomes noticeable. The actual form of the temperature dependence can then be described by an equation of the form of Eq. (6), which assumes that the two contributions are additive.

The master curves for the dynamic data cover a total frequency range of twelve decades. Over this entire range the viscoelastic properties change by less than 1.75 decades. The two ends of the range mark the beginnings of the 1,4-polybutadiene and the polystyrene transitions, respectively. We therefore have an enormously extended range of frequencies (5 - 6 decades from $\log \omega = -1$ to 5) over which the material properties hardly change at all. This is the region between the two transitions. In this region the pseudorubbery modulus is about 30 bars (or 435 psi). The loss modulus also remains virtually constant over the same region.

The storage compliance shows essentially the same features as the modulus. The loss compliance appears to rise towards the expected polystyrene peak at the lower frequencies while the loss modulus appears to rise towards the polybutadiene peak at the higher frequencies. If this interpretation is correct, the loss compliance peaks for both transitions appear at higher frequencies than do the peaks in the loss moduli. This is contrary to what is observed, for the loss peaks in amorphous linear homopolymers in accordance with the linear theory of viscoelasticity. At frequencies below about $\log \omega = -2$ there is a sudden unexplained drop in the loss modulus.

The dynamic data calculated from the step response functions show the same broad features except that the pseudorubbery modulus region here extends even further over about

twelve decades (from about $\log \omega = -3$ to about 9). There is a small peak in $\log G''(\omega)$ at $\log \omega = -4$, a little below the region in which the loss modulus obtained in the dynamic measurements shows the unexpected drop. The peak is undoubtedly real since it is present in both the relaxation and creep curves. It appears to be too small to represent the damping peak of the polystyrene.

Turning now to the damping curve, Fig. 8, the polybutadiene peak is approached at the higher frequencies. In the dynamic measurements it either occurs at lower frequencies than in the creep and relaxation measurements or is more pronounced. At the lower frequencies a rather broad low peak appears in the dynamic measurements at around $\log \omega = -3$ which appears to be shifted to even lower frequencies in the relaxation and creep measurements. The damping is practically constant over about ten decades of frequencies from about $\log \omega = -4$ to 6 for the dynamic measurements, and to even higher frequencies in the relaxation and creep measurements. The amount of damping, however, is small, $\log \tan \delta$ being of the order of -0.6 for the dynamic measurements, and -1.0 for the relaxation and creep measurements.

The diblock, SB 40/160, shows an entirely different behavior. The temperature dependence shown in Fig. 13 could be fitted by a WLF equation with $c_1 = 2.84$, $c_2 = 55.7^\circ\text{C}$ at the reference temperature of 25°C . This equation predicts values of $\log a_T$ which are not too different from those obtained by the equation of Saunders, Ferry, and Valentine³² with $c_1 = 6.23$ and $c_2 = 72.5^\circ\text{C}$ at the same reference temperature. At temperatures above about 30°C the empirical shift factors deviated from the behavior predicted by the WLF equation. However, when the differences are plotted against the reciprocal temperature a straight line such as that in Fig. 14 is not obtained. Shifting of the data at the higher temperatures (the region of lower frequencies) was fairly difficult as may be seen from the scatter of the data in Figs. 9 through 12. At the three lowest temperatures (i.e. in the region of the highest frequencies) the empirical shift factors are also ambiguous. These weight the WLF parameters quite heavily. A decision whether an equation such as Eq. (6) is applicable must be deferred until more precise data are obtained at lower frequencies where the measurements are particularly difficult to make because of the stiffness of the specimens.

The master curves, Fig. 9 to 12, show the transition region of the 1,2-polybutadiene moiety. No extended plateau develops here between the two transitions, partly because they are spaced more closely and also because there are no glassy crosslink points in the diblock. Rather, the glassy polystyrene domains act as junctions for star-like clusters. Because of the absence of crosslinks the material flows more easily than the

triblock even though its molecular weight is larger. The fanning-out of the data at frequencies below about $\log \omega = 5$ could indicate a change in viscosity as a function of temperature, perhaps as a consequence of progressive dissociation of the clusters. An attempt to derive the temperature dependence of the viscosity by shifting the real part of the complex viscosity, $\eta'(\omega)$, failed because of the insufficiency of the data.

The temperature dependence of the viscoelastic properties of block copolymers can be expected to be essentially similar to that of polymer blends. Horino et al.⁶ have examined blends of polyvinyl acetate with polymethyl methacrylate. The temperature dependence of these blends was qualitatively similar to the behavior of the block copolymers reported here. The Japanese workers considered the temperature dependence on the assumption that the free volumes of the constituents are additive. Although this assumption is useful in case of random copolymers,^{3,4,5} there is no basis for it in either blends or block copolymers because the constituents form separate domains.

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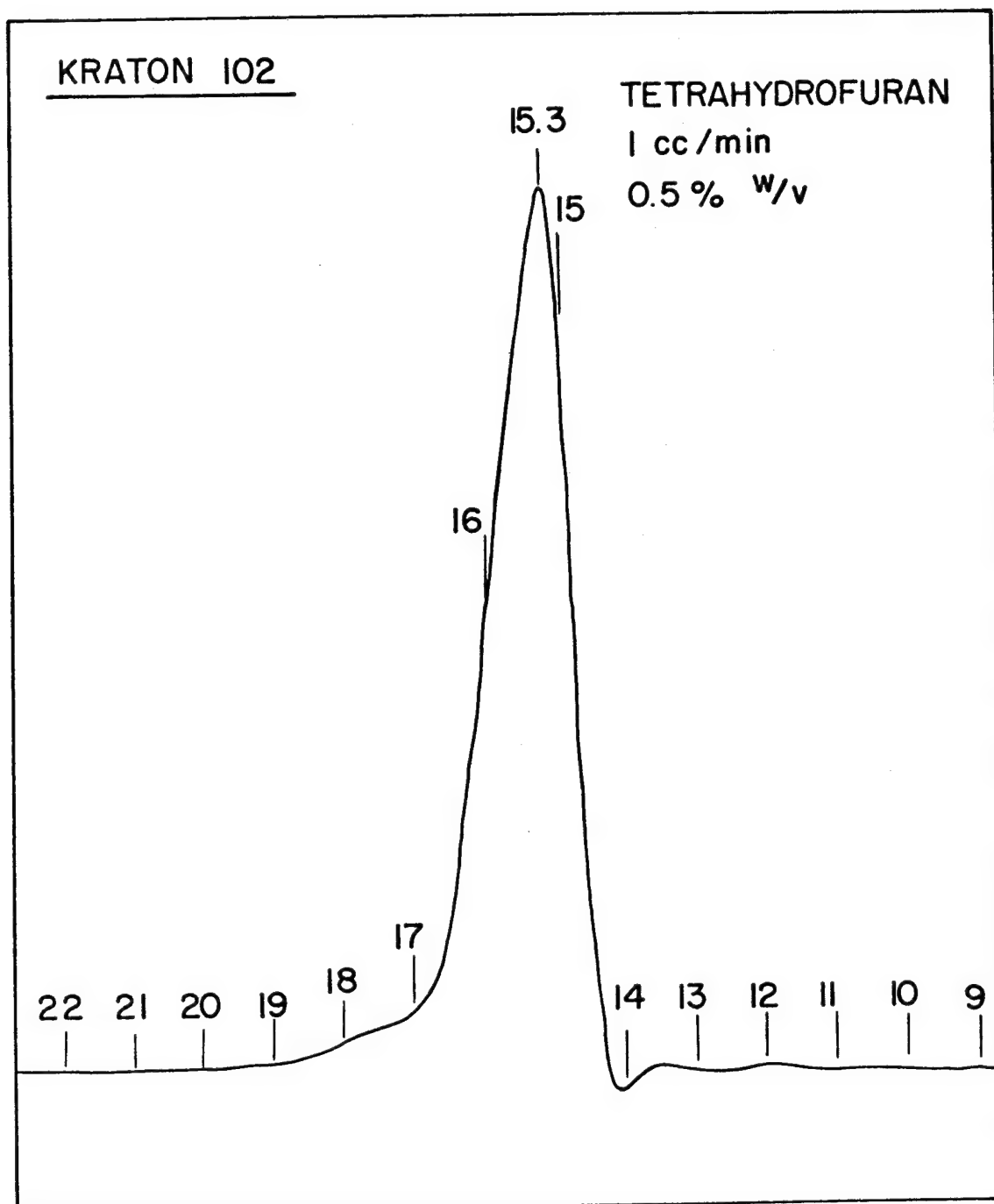


Figure 1. Gel Permeation Chromatogram of Kraton 102
(0.5% w/v in Tetrahydrofuran).

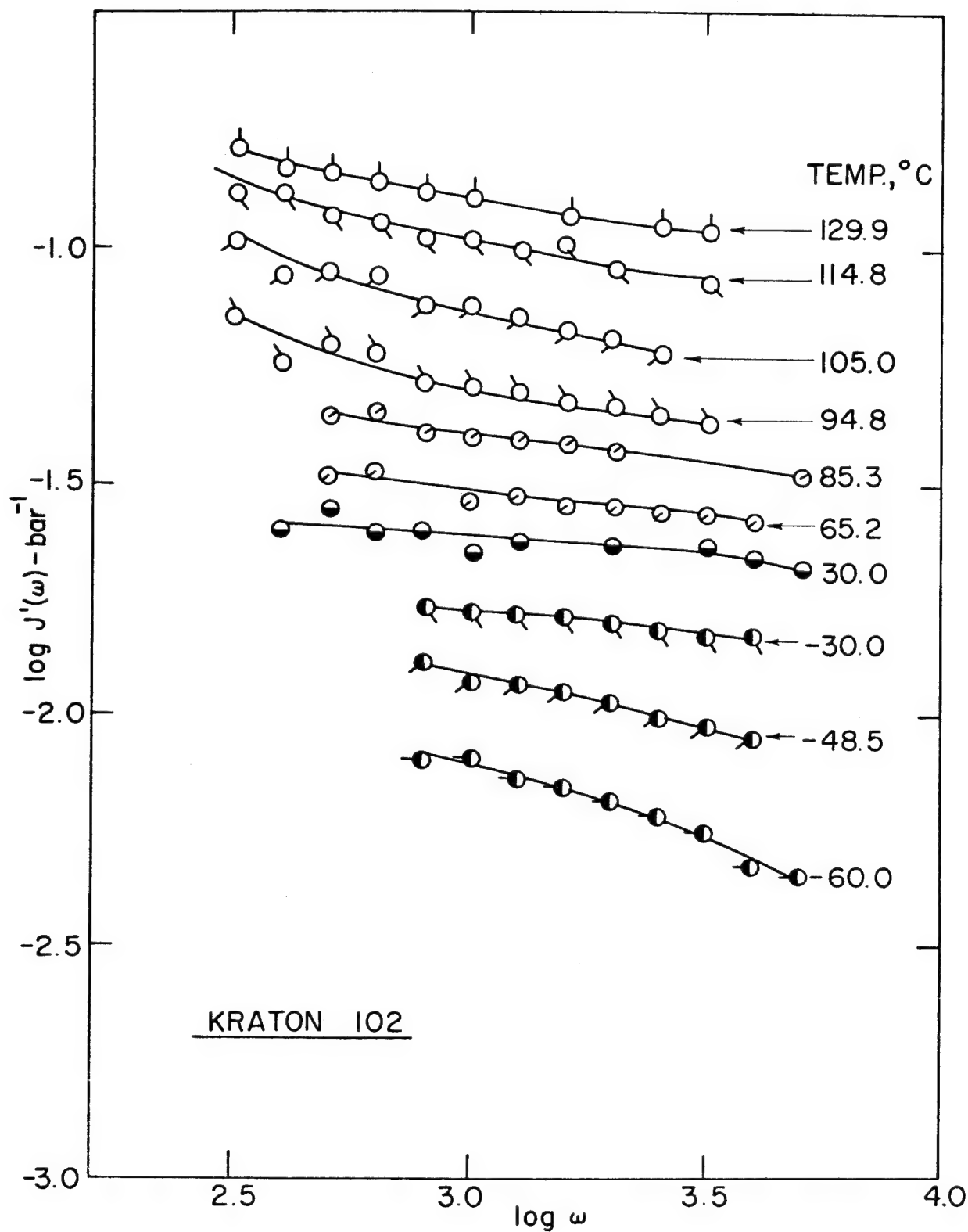


Figure 2. Storage Compliance, $J'(\omega)$, of Kraton 102 at Different Temperatures as Function of the Radian Frequency, ω_T .

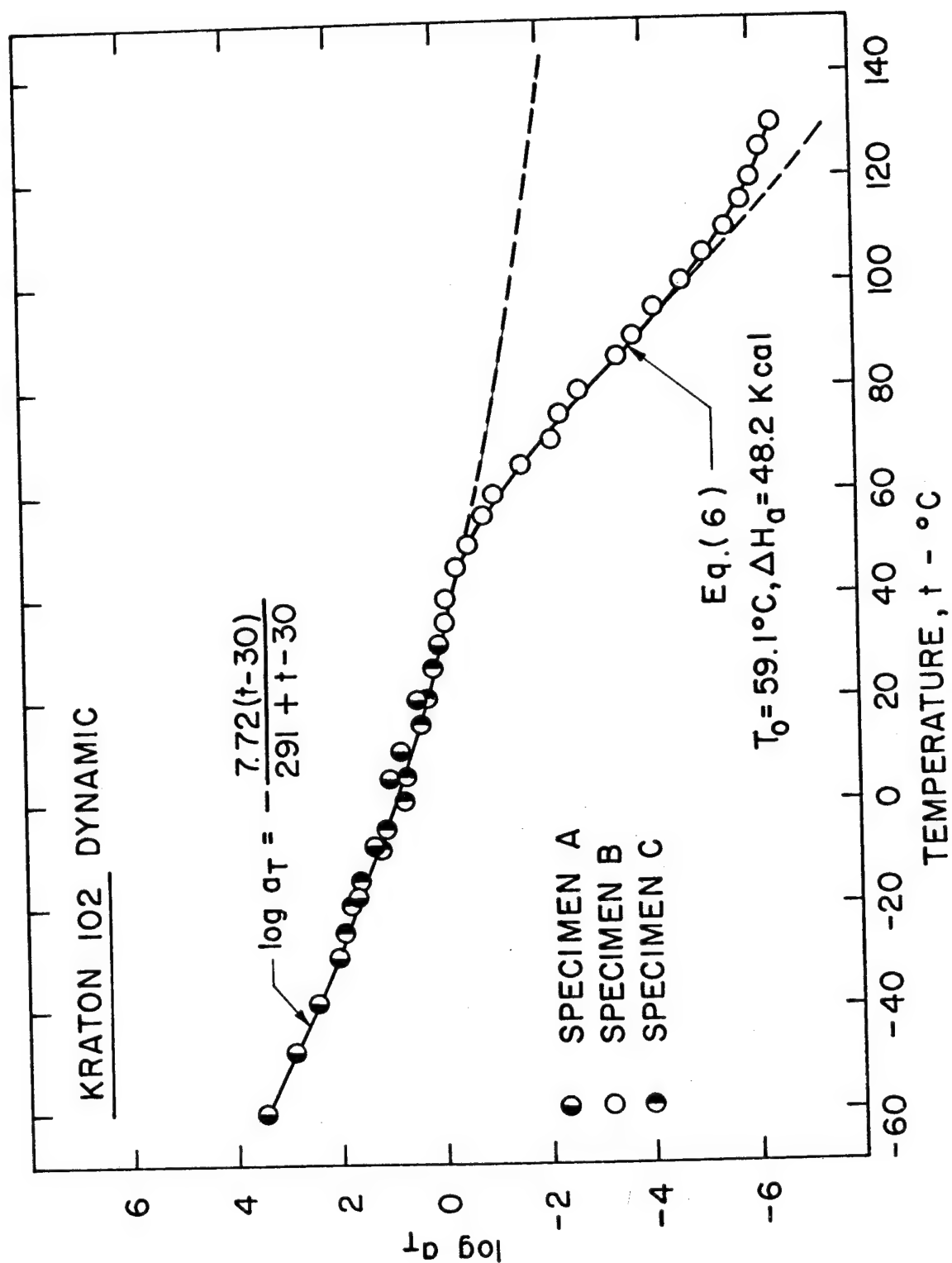


Figure 3. Temperature Dependence of Dynamic Measurements Obtained on Kraton 102.

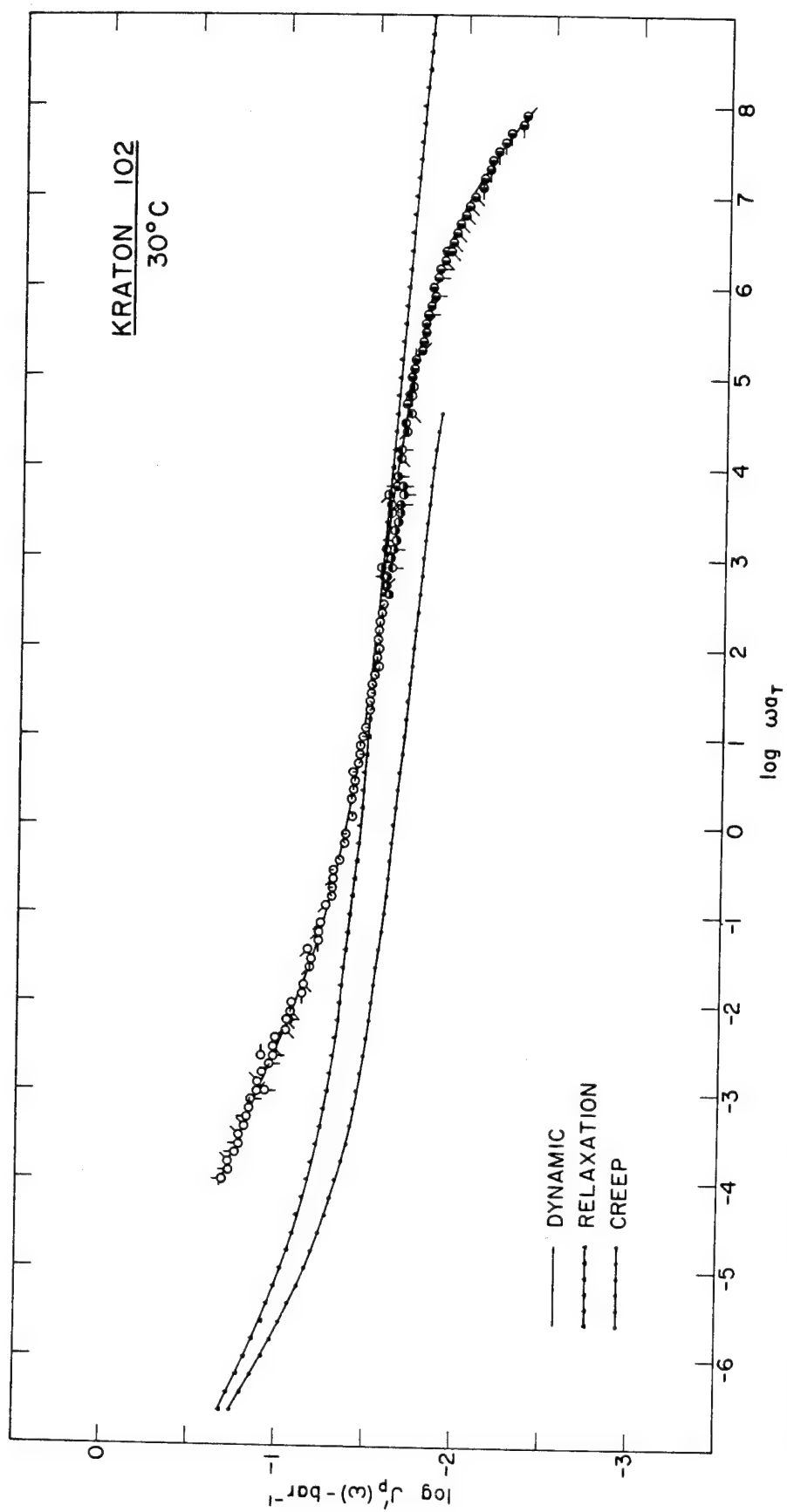


Figure 4. Master Curves of the Storage Compliance, $J_p'(\omega)$, of Kraton 102 as Function of the Radian Frequency, ωa_T , at 30°C.

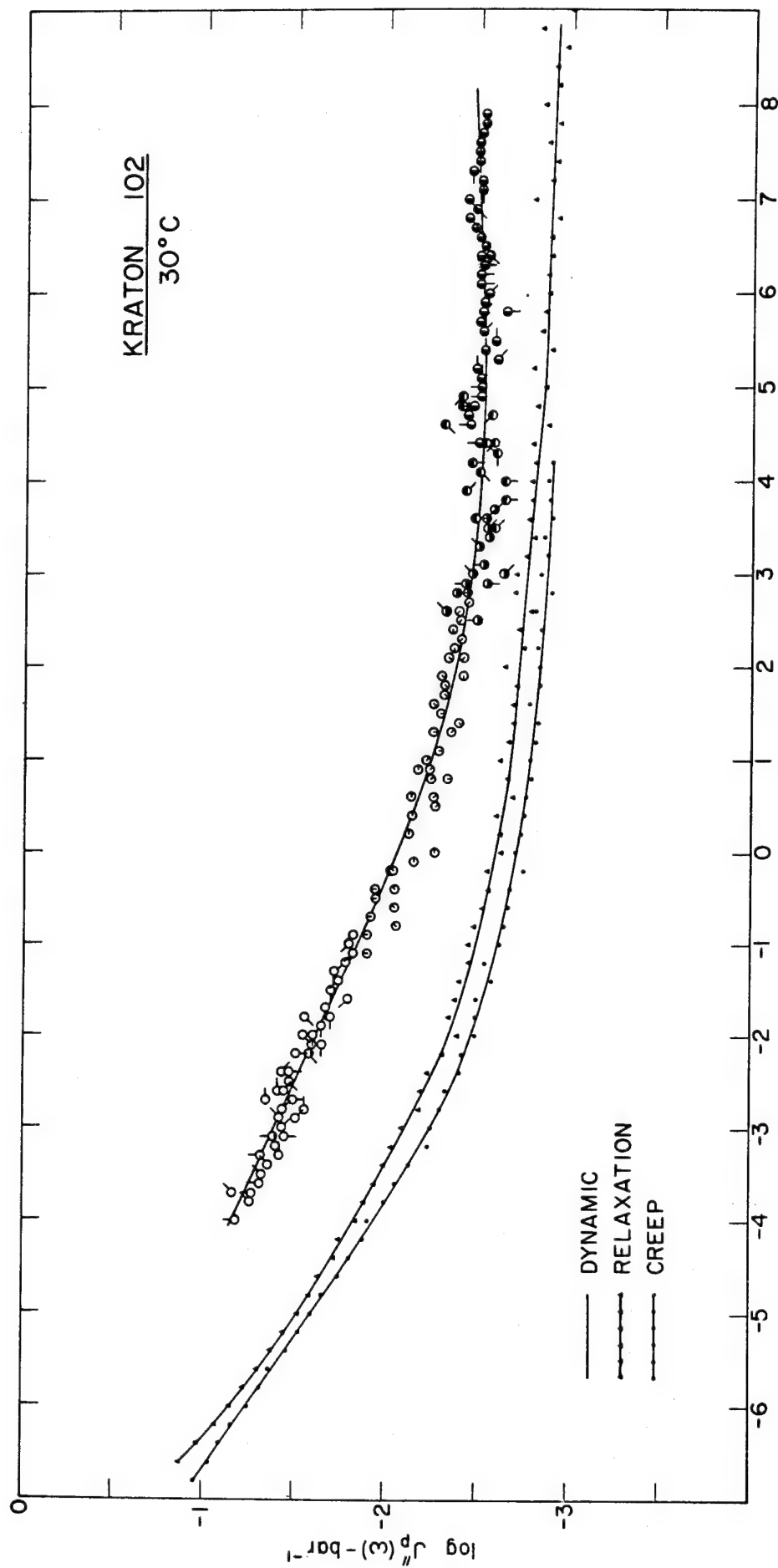


Figure 5. Master Curves of the Loss Compliance, $J_p''(\omega)$, of Kraton 102 as Function of the Radian Frequency, ωa_T , at 30°C.

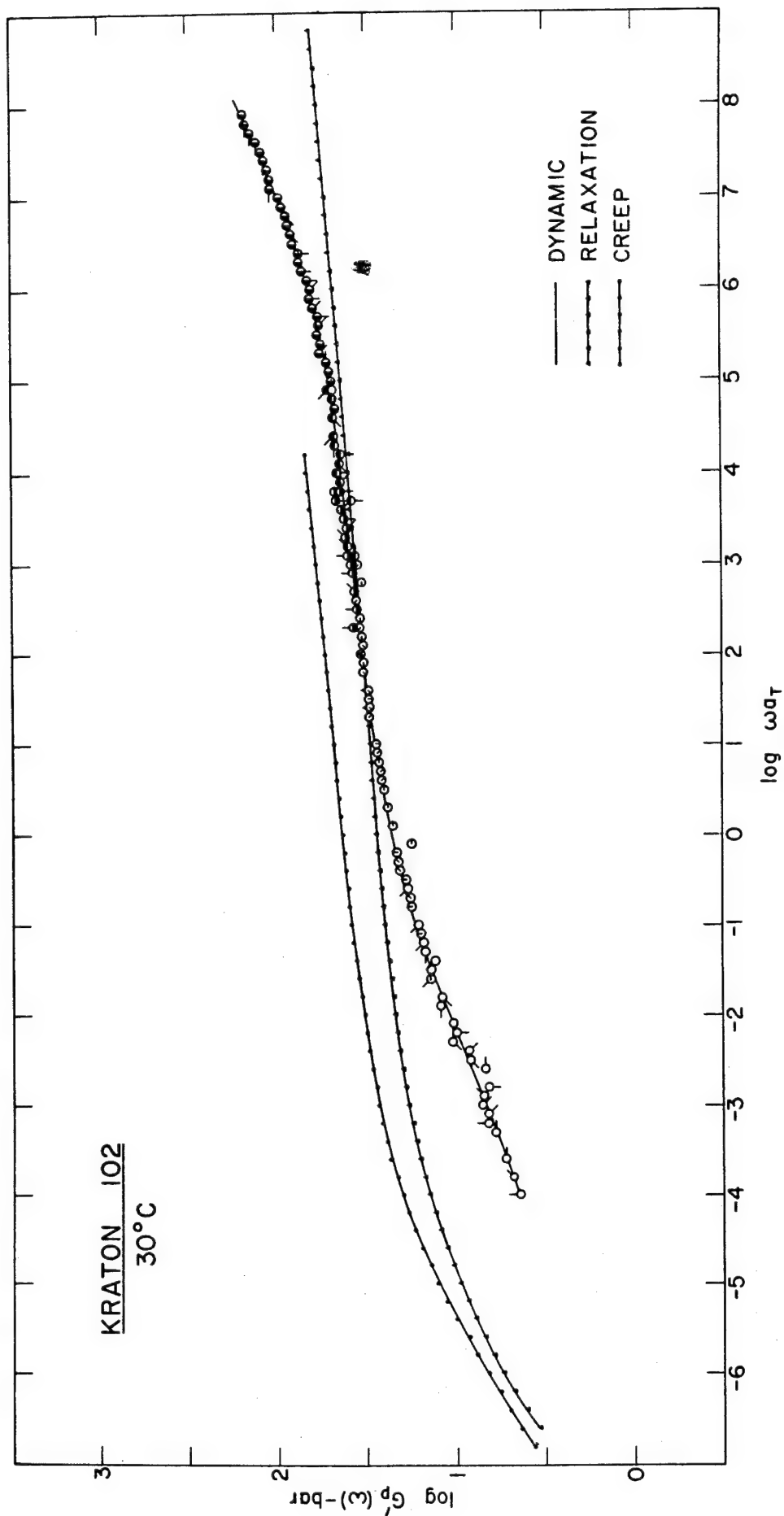


Figure 6. Master Curves of the Storage Modulus $G_p'(\omega)$, of Kraton 102 as Function of the Radian Frequency, ωa_T , at 30°C.

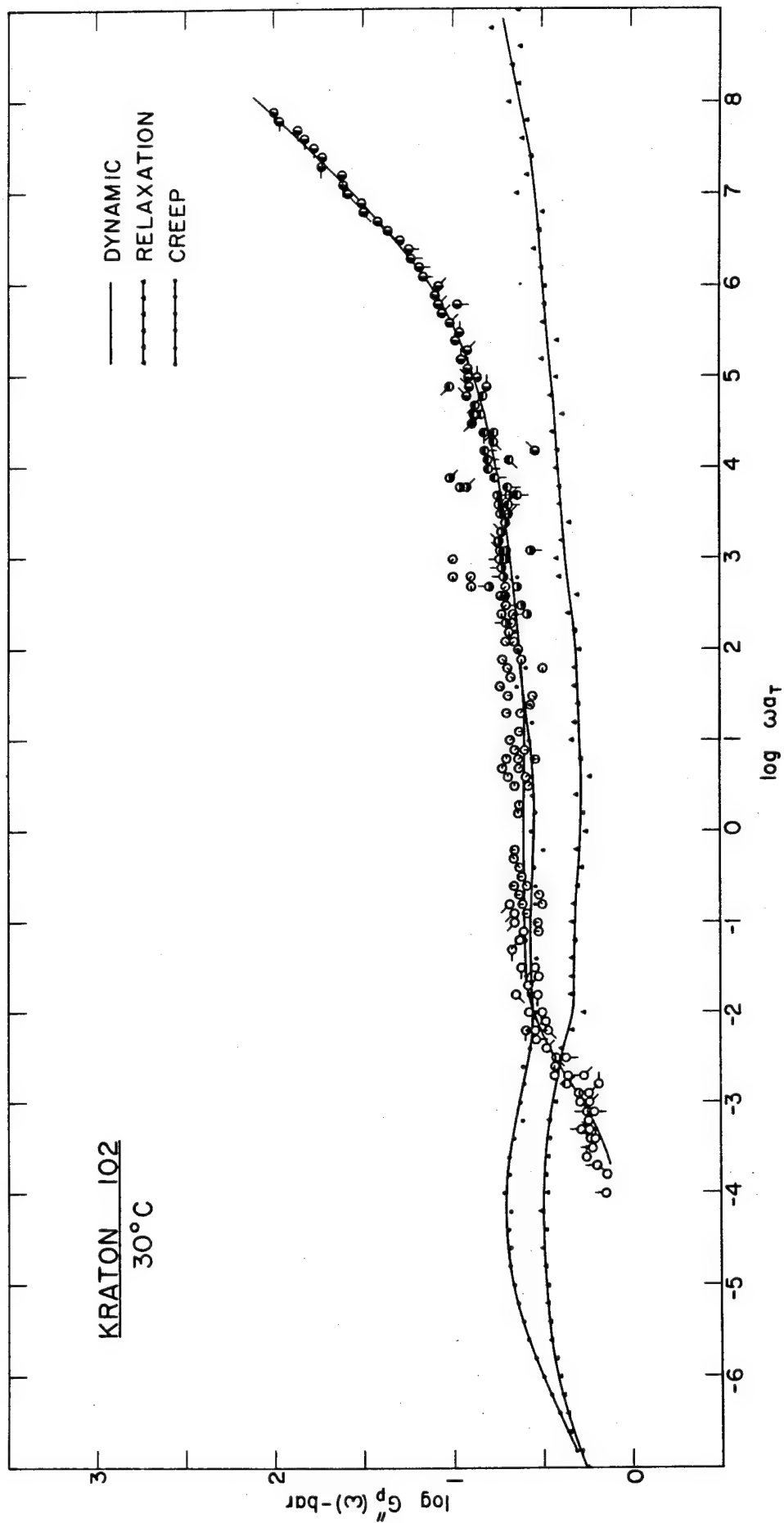


Figure 7. Master Curves of the Loss Modulus, $G_p''(\omega)$, of Kraton 102 as Function of the Radian Frequency, ωa_T , at 30°C.

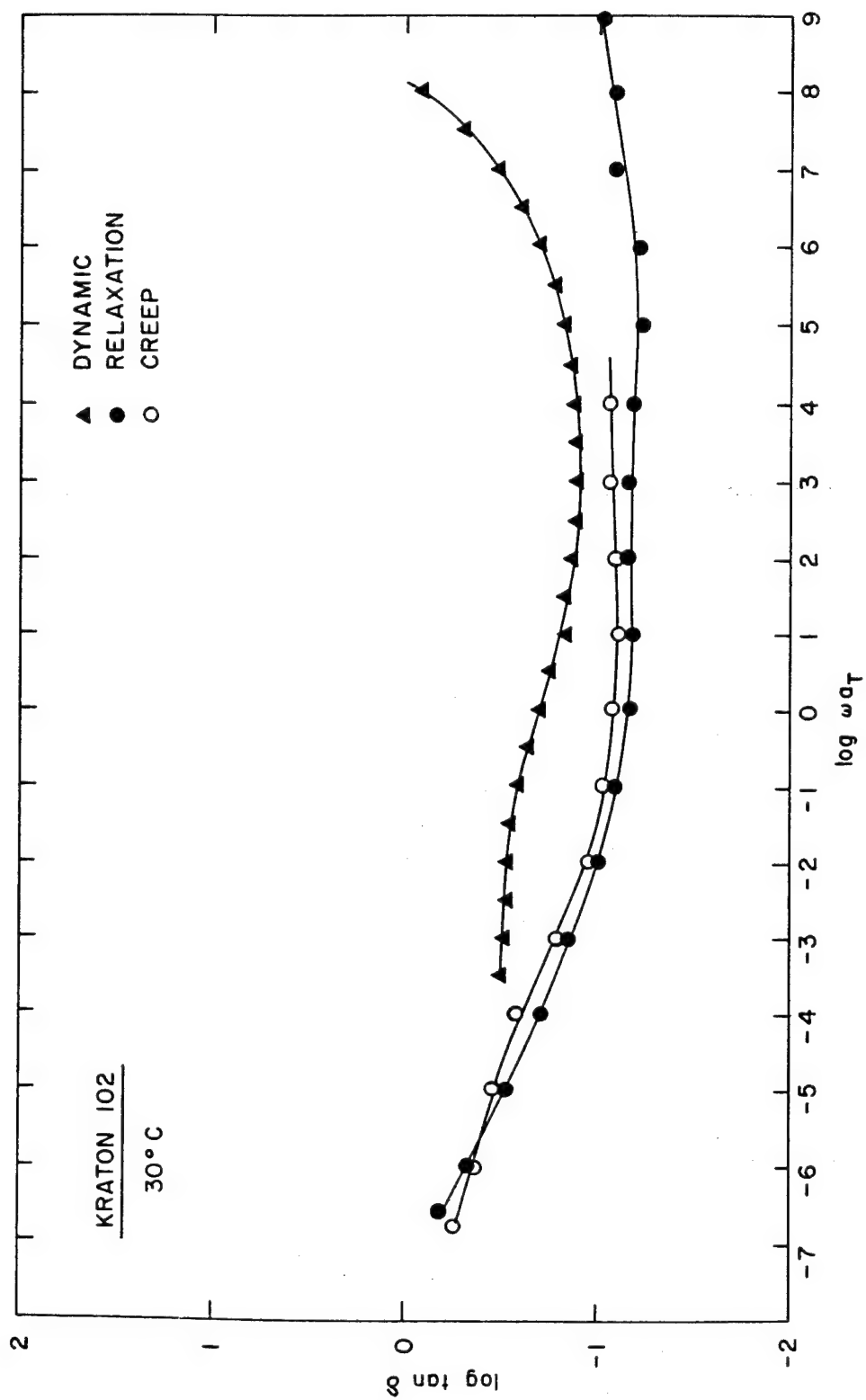


Figure 8. Loss Tangent Curves for Kraton 102.

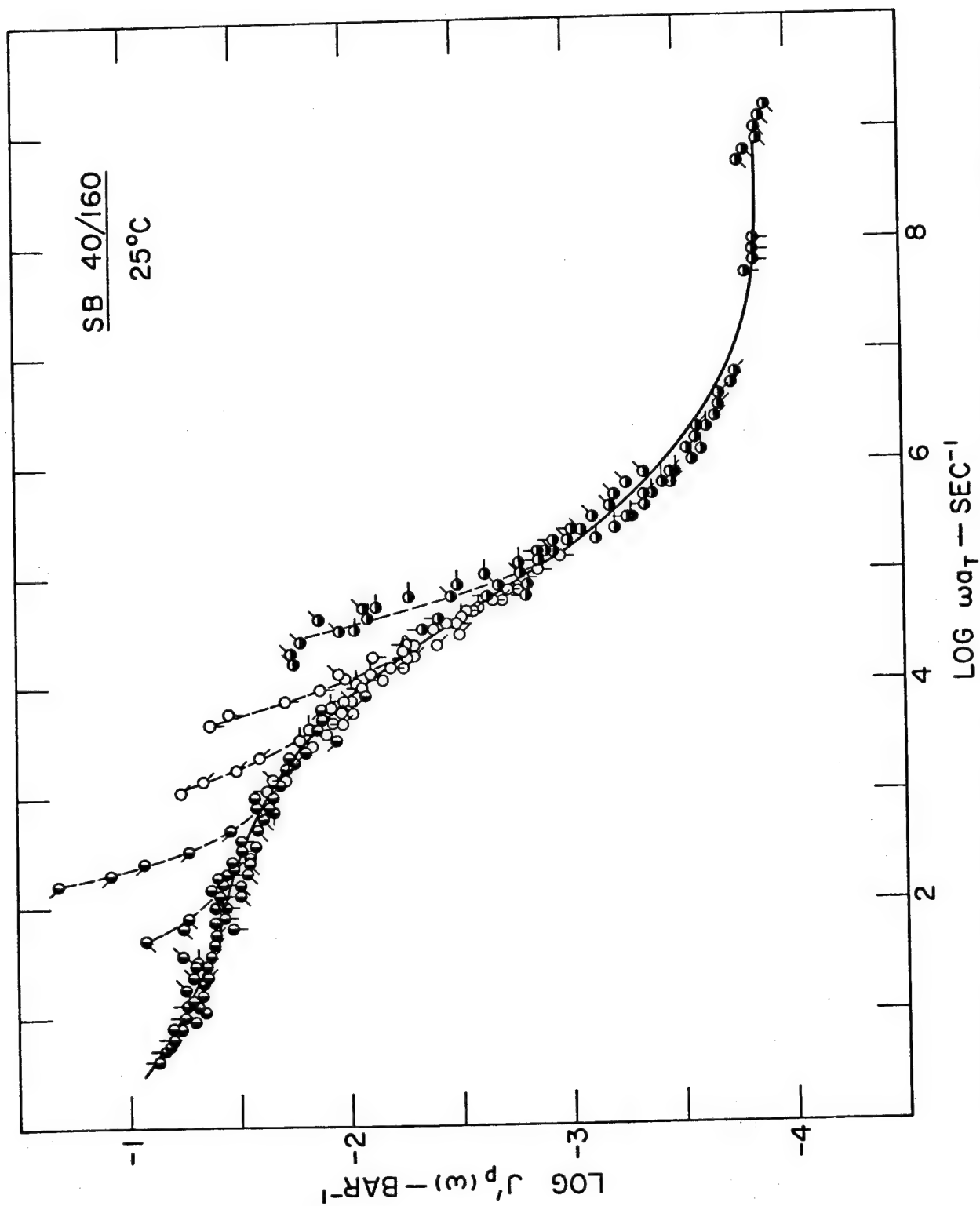


Figure 9. Master Curves of the Storage Compliance, $J_p'(\omega)$, of SB 40/160 as Function of the Radian Frequency, ωT , at 25°C.

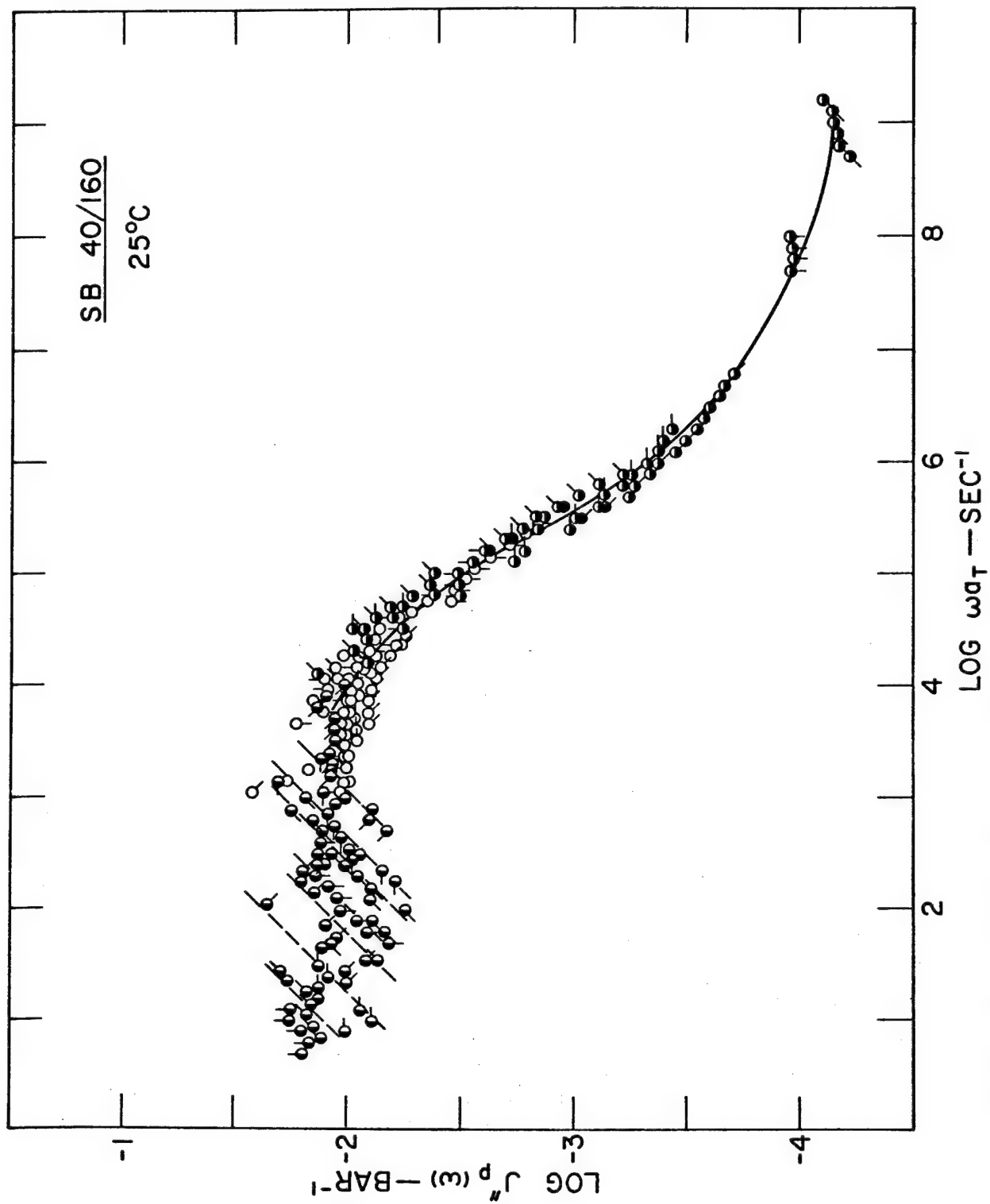


Figure 10. Master Curves of the Loss Compliance, $J_p''(\omega)$, of SB 40/160 as Function of the Radian Frequency, ωa_T , at 25°C.

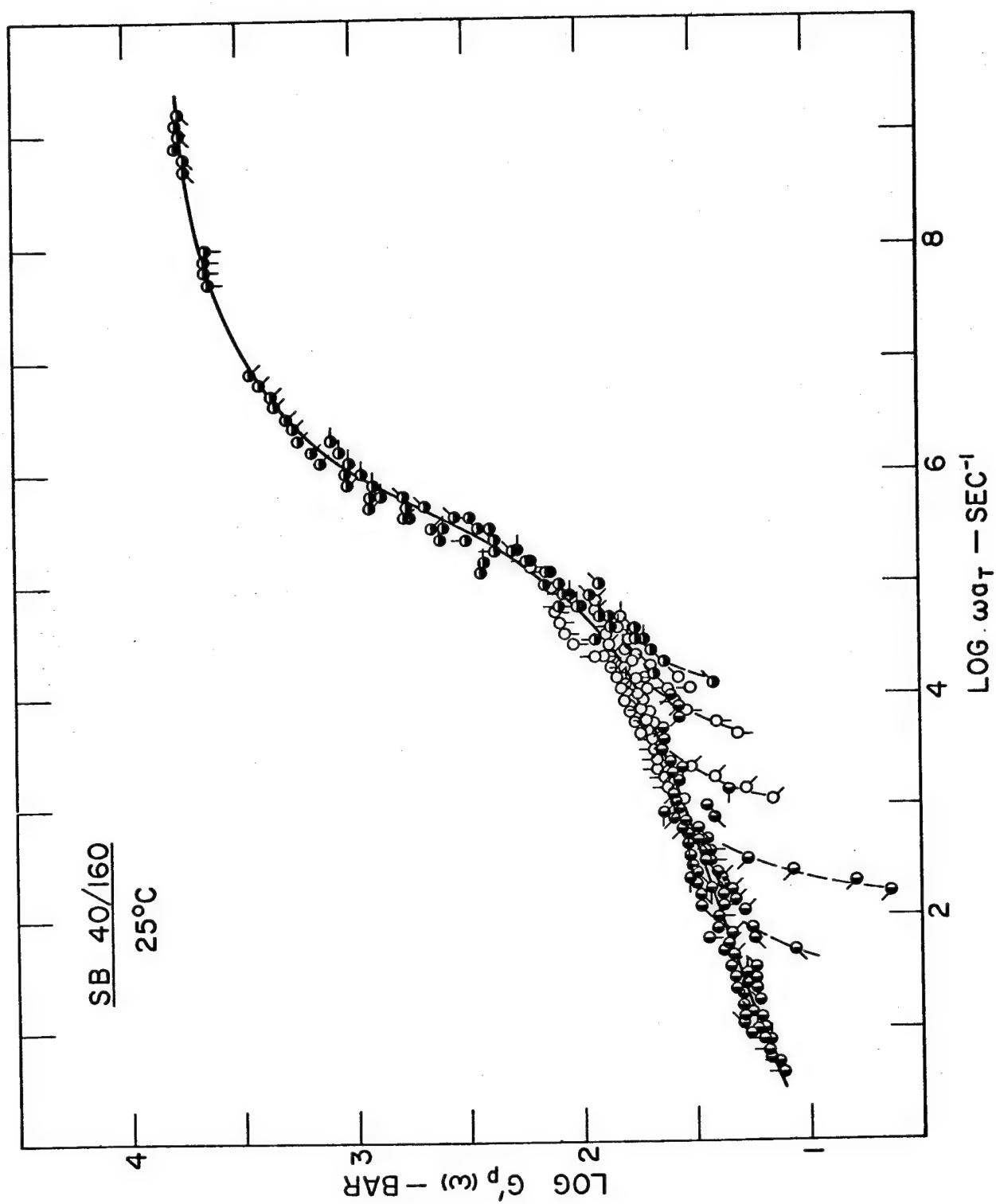


Figure 11. Master Curve of the Storage Modulus, $G_p'(\omega)$, of SB 40/160 as a function of the Radian Frequency, ωa_T , at 25°C.

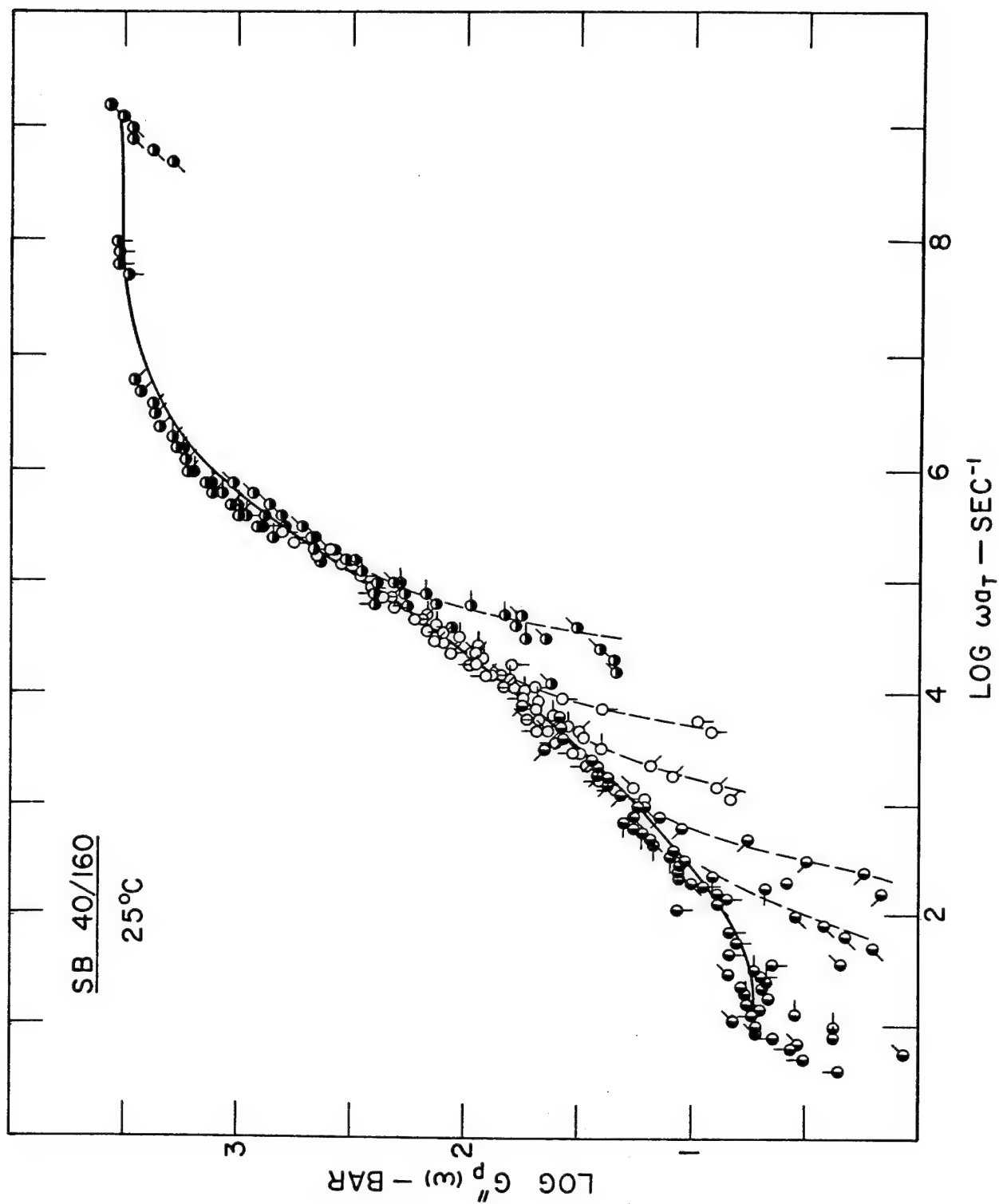


Figure 12. Master Curve of the Loss Modulus, $G_p''(\omega)$, of SB 40/160 as Function of the Radian Frequency, ωa_T , at 25°C.

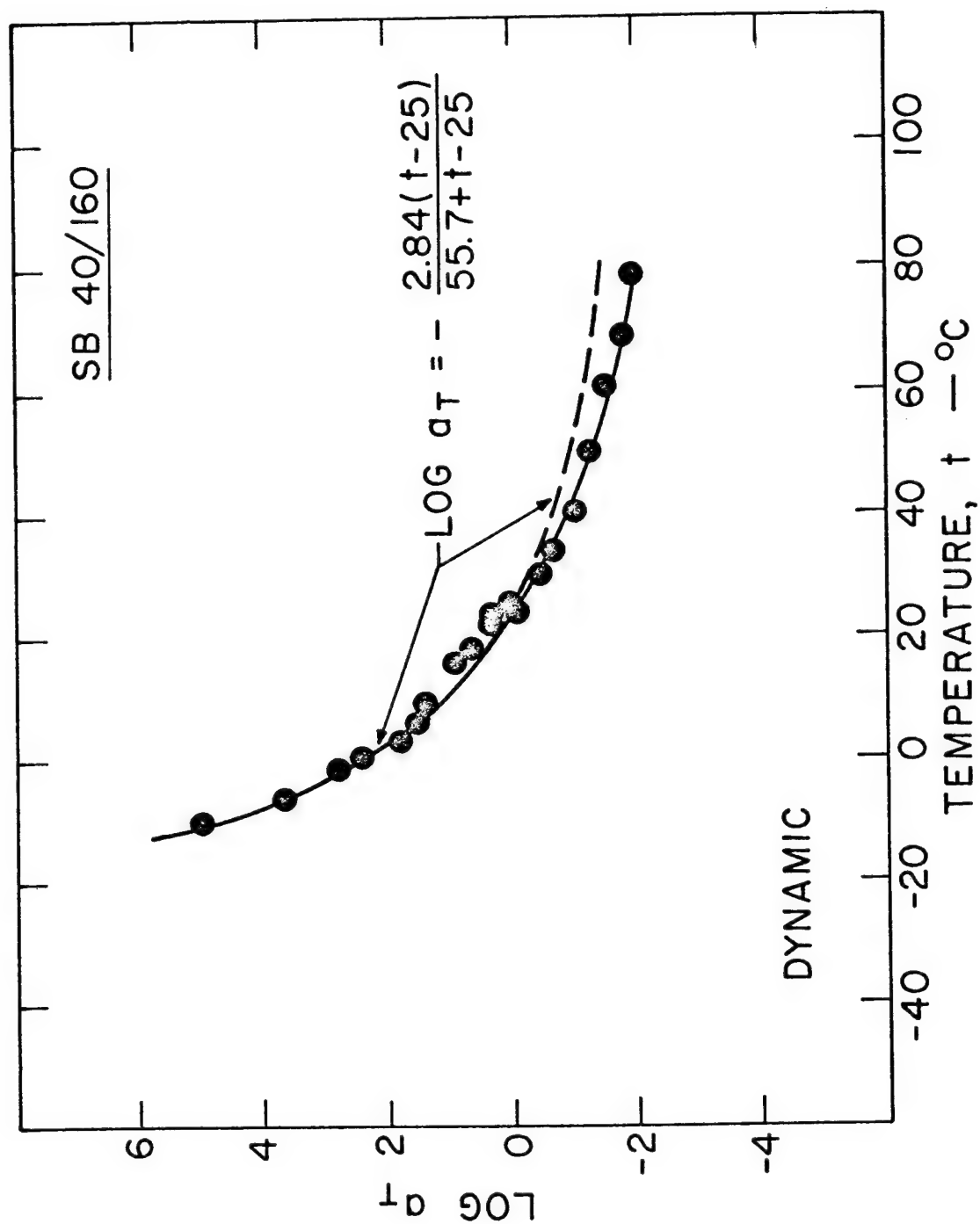


Figure 13. Temperature Dependence of the Dynamic Measurements
Obtained on SB 40/160.

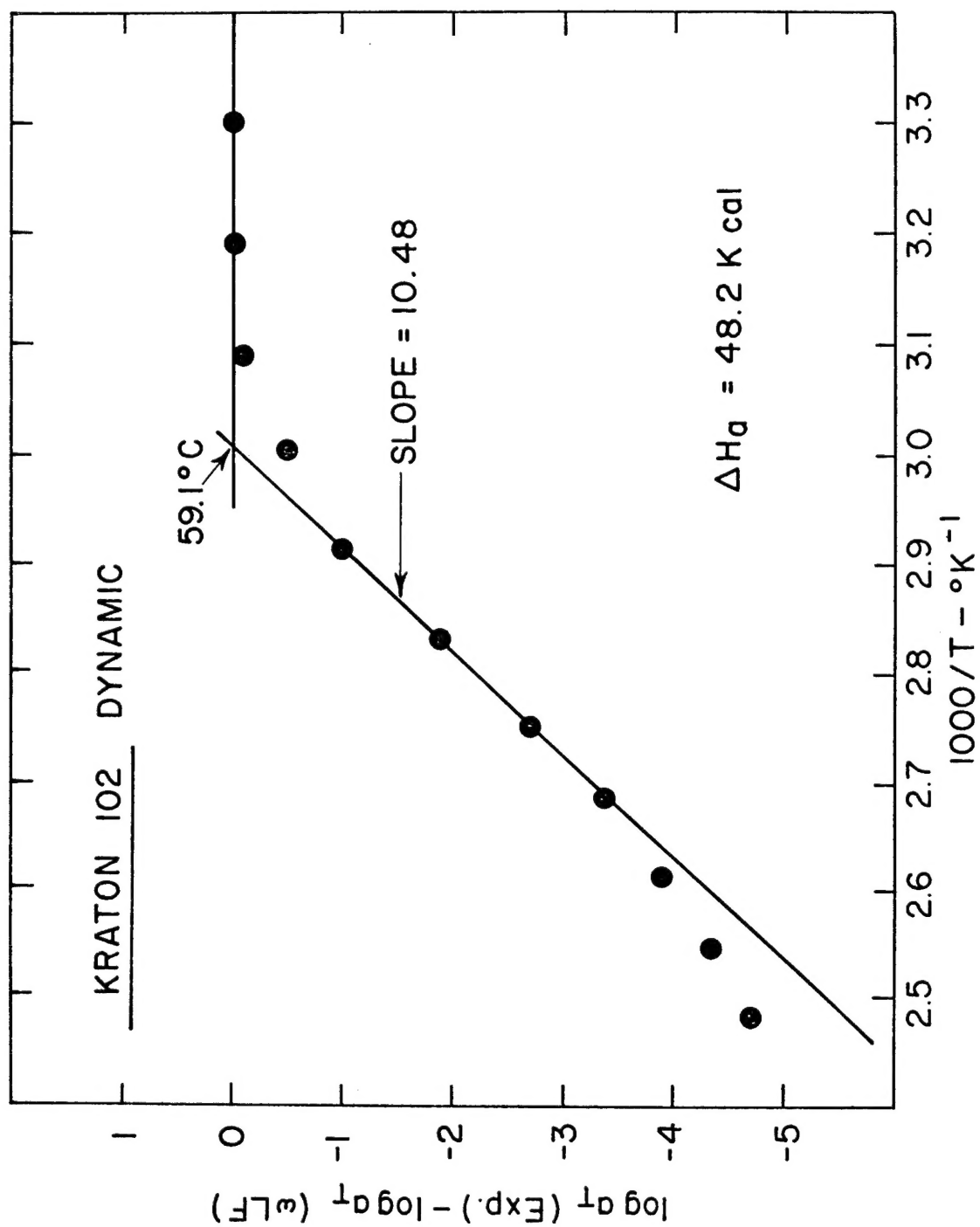


Figure 14. Difference between the Empirical Shift Factors, log a_T (EXP.), and those given by Eq. (5), log a_T (WLF), Plotted against the Reciprocal Absolute Temperature. (Dynamic Data on Kraton 102).

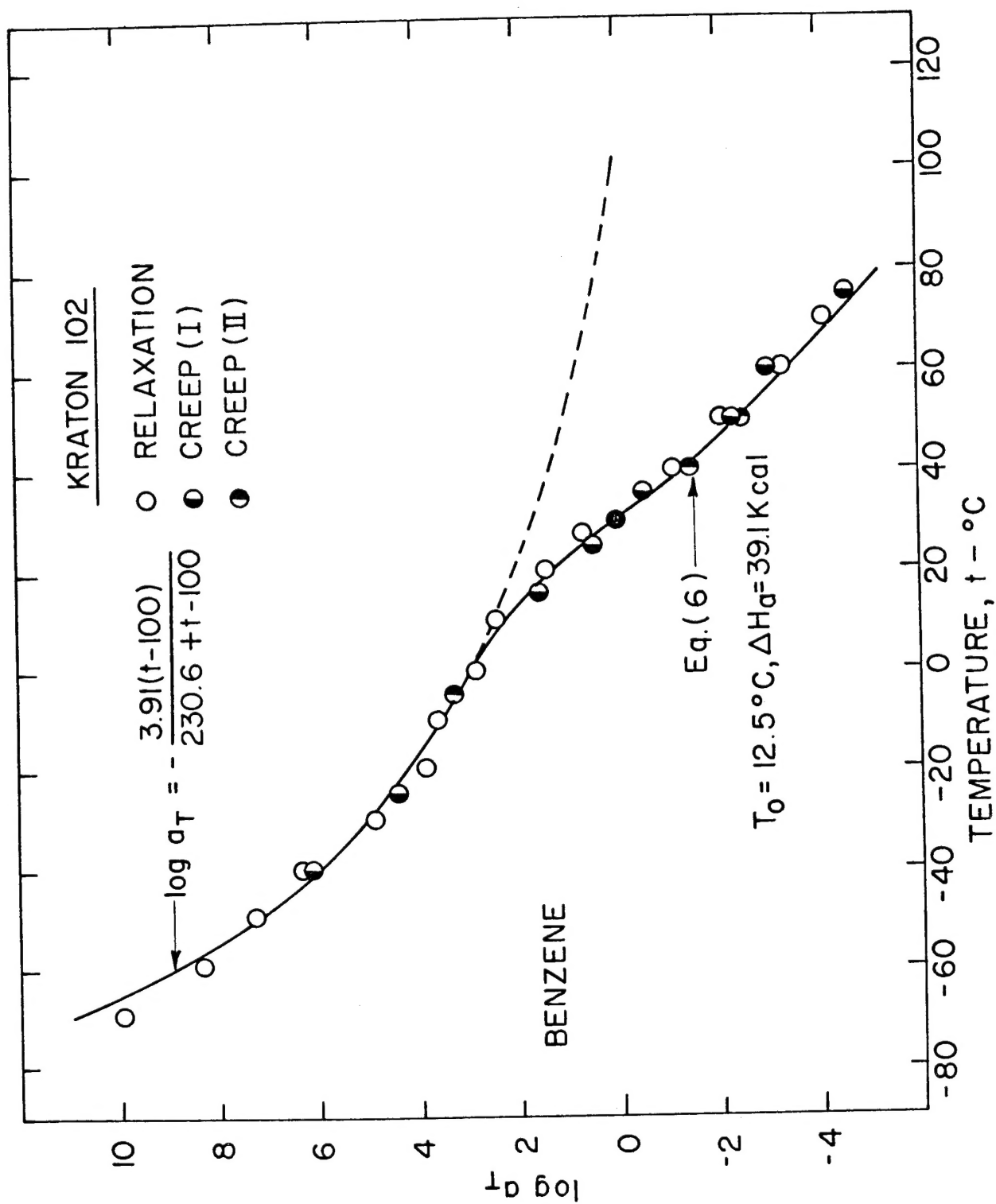


Figure 15. Temperature Dependence of the Relaxation and Creep Data Obtained on Kraton 102 Cast from Benzene Solution.

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13. ABSTRACT The mechanical properties of a polystyrene - 1,4-polybutadiene - polystyrene block copolymer of molecular weight 9500/37500/9500 were determined at temperatures between -60 and 130°C in sinusoidal shear over a frequency range from 25 to 1250 Hz, in tensile stress relaxation from -70 to 70°C over a time scale ranging from 1 to 1000 sec. and in tensile creep from -40 to 75°C over a time scale from 10 to 10,000 sec. The dynamic mechanical properties of a 1,2-polybutadiene - polystyrene block copolymer of molecular weight 160,000/40,000 were measured at ten temperatures, between -10 and 80°C over a frequency range from 250 to 2500 Hz. A firm mathematical and theoretical foundation was established which is essential for the continued development of energy absorption materials.			

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